SELECTED PAPERS ON

# SILICIES ELASTONEAS

Volume 2

## Abstracts

#### Silicone Rubber-A Perspective

#### 硅橡胶一展望

文章概述了硅橡胶的发展历史、聚合、加工工艺、性能改进、新品种的发展与应用。重点介绍了对硅橡胶低温性能、机械性能 和抗辐照性能等方面的研究工作。

#### Silicone Rubber

#### 硅橡胶

详细讨论了硅橡胶在工程上的用途,介绍了它们固有的特性,在极端温度下的操作性能、耐化学特性及机械性能,并考虑了硅弹性 体在就地密封上的应用。

## Élastomères de Silicones Propriétés et Applications

#### 硅橡胶的性能与应用

本文列举了近20年来硅橡胶品种的发展,这种发展开拓了硅橡胶的使用范围。也举了硅橡胶和其它橡胶老化情况的对比。以 及硅橡胶在不同溶剂中性能变化的情况。

# Кинетина и механизм окислительной деструкции полидиметилсилоксановых каучуков

#### 整二甲基硅橡胶的氫化降解动力学和机理

根据动力学原理研究了以二枯基过氧作氧化引发剂,以N-苯基-β-萘胺作氧化抑制剂的硅橡胶的氧化降解机理。

# Озонное старение резин из силоксановых научуков

#### 硅橡胶的臭氧老化

文章研究了各种硅橡胶在高浓度臭氧作用下的物理机械性能(抗张、伸长和永久变形)的变化和最大体膨值。

# Влияние строения сшивающих агентов на механические свойства ненаполненных силиконовых композиций, вулканизованных по реакции "полиприсоединения"

## 交联剂结构对无填料"加连剂"硫化硅橡胶机械性能的影响

介绍了几种以含氢硅油作交联剂的硅橡胶的化学结构。列表指出了不同结构交联剂对胶料硫化速度和机械性能的影响。重点指 出:当采用大约相等量的 SiH 基时,以二甲基氢硅链节封端的交联剂组成的胶料化三甲基硅链节封端者具有较快的硫化速度和较好 的机械性能。

# О процессах, протекающих в кремнийорганических композициях, вулнанизуемых влагой воздуха 借助于空气中水分进行硫化的硅橡胶反应机理

根据三度缩聚理论对单组份RTV硅橡胶在空气中与水分接触后产生的硫化反应作了探讨。提出了在反应前期可能形成的化合 物模型,以及可以用来解释该组成物特点的硫化反应机理。

## Влияние строения ортаносилилонсимных сшивающих агентов на скорость отверждения силоксановых каучуков и физико-механические свойства вуяканчзатов

# 有机硅肟结构对硅橡胶固化速度和硫化胶物理机械性能的影响

文章指出硅橡胶的硫化速度以及硫化胶的物理机械性能取决于有机硅肟类硫化剂的结构。至于硫化活性则与电负性取代基结构 和硅原子上的水解基团的碱性强弱有关。

# 高强度シリコーンゴム组成物

#### 高强度硅橡胶组成物

介绍高强度硅橡胶的制备方法。每100份可热硫化的硅橡胶中加入5~30份经过硅氧烷处理的聚酯纤维。硫化剂二氯过氧化苯 甲酰是事先与硅油调成膏状使用的。

## Thermoplastverstärker Siliankautschuk Eigenschaften und Anwendungsgebiete 热塑性塑料增强的硅橡胶的性能和应用范围

这是一种热塑性的硅橡胶,经适当的合成与加工而制得。本文讨论其组分与结构、生胶粘度、机械性能、耐热性能和电性能以及其用途。

#### ゴム成形品の制造方法

#### 橡胶制品的制造方法

本文采用部份硫化硅橡胶经骤冷、伸张、再在张力下进一步硫化等步骤制得。此高强度硅橡胶胶料由硅橡胶与 DCP 组成。以  $150~{\rm kg/cm^2}$  压力加压制成 2mm 厚的胶板,再在  $100^{\circ}{\rm C}$ 加热  $10~{\rm C}$ 钟后放在水中骤冷,伸长 500%,在不解除张力情况下经  $200^{\circ}{\rm C}$  烘箱加热  $80~{\rm C}$ 钟,可制得强力为  $186{\rm kg/cm^2}$  伸长率为 100% 的产品

# Reinforcement of Silicone Rubber By Particulate Silica

#### 用细粒子白炭黑增强硅橡胶

通过不同方法对气相白炭黑表面进行处理,并研究白炭黑表面与硅橡胶表面之间的相互作用。处理效果是通过结合橡胶量来测定的,结果表明这种相互作用大大超过烃类橡胶,并指出如使用羟基封端的硅橡胶则此种相互作用可以达到极点。

# Process and Compositions of Rubber Vulcanizates Wirth Silicone Polymerizates 硫化胶和硅聚合物的工序和组合

介绍在硅橡胶胶料中加入氧化铝或碳化硅作增强填料,可提高硫化胶的耐磨性能,具伸长率仍不低于400%。

#### High Strength Organopolysilexane Compositions

#### 高强度有机聚硅氢烷组成物

本专利采用高粘度和低粘度乙烯基硅橡胶并用,在室温或高于室温的条件下进行固化,硫化胶性能可达到如下水平:

强力 70公斤/厘米2

伸长率 1000%,

硬度 23 抗撕强度

26.8 公斤/厘米

# Novel Organofunctional (ketoximino) Silanes & Room Temperature Vulcanizable Compositions Containing the same

# 新生有机官能(酮肟基)硅烷及含有该硅烷的室温硫化硅橡胶组份

介绍了三甲乙酮肟基乙酰氧基乙基硅烷的合成方法以及其作为羟端基聚二甲基硅氧烷的室温硫化剂时的硫化特性。

#### 常压热气加硫可能な导电性シリコーンゴム组成物

#### 常压热空气硫化导电硅橡胶组成物

采用双(2,4-二氯苯酰)过氧作交联剂,填充乙炔和炭纤维。成品的体积电阻为 50 欧姆-厘米。

#### Easier Faster Processing With Powdered Silicone Rubber

#### 用粉末硅橡胶达到简速加工过程

介绍杜康宁公司生产的一种粉末状硅橡胶,对它的贮存性,机械性能,操作安全性以及加工特性都有简述,可供注压成型和压缩成型。

# Über Herstellung und Eigenschaften von heterogenen Ionenaustauschermembranen unter Verwendung von Silikongummi

#### 硅橡胶离子交换灌溉的制法

介绍一种电化学性能和机械性能优良的硅橡胶离子交换薄膜的制造方法及其性能。

# Drucklose Kontinuierliche Vulkanisation von silikonkautschukprotilen

#### 硅橡胶材料的无压连续硫化

介绍一种能供硅橡胶连续硫化使用的立式和卧式红外线加热装置。

#### プライマー組成物

# 硅橡胶与金属耐热结合用的表面处理剂

该表面处理剂的组成为: 聚(二甲基硅氧烷)100,含 0.1 乙烯基/Si 的聚(甲基乙烯基)硅氧烷 50,乙烯基三( $\alpha$ -甲氧基乙氧基)硅烷 50,磷酸 2,甲苯 600,异丙醇 200。

本处理剂可耐热 250°C。

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#### シリコーン系接着剤および一シリング材

#### 硅系胶點剂及密封材料

文章介绍了硅体系的胶粘剂和密封赋子材料,重点介绍了单组份室温固化型硅橡胶胶粘剂及赋子的类型、反应机理及特点。并介绍了日本现有的硅橡胶腻商品牌号。

#### 室温加硫性シリコーンゴムの制造

#### 室温硫化硅橡胶的制造

介绍一种由美国杜康宁公司申请的钛化物作催化剂的室温固化硅橡胶。

# Low Modulus Room Temperature Vulcanizable Silicone Elastomer With Improved Slump Characteristics 低模数及改善了抗塌陷性的室温硫化硅橡胶弹性体

本专利介绍采用羟基封端的二甲基聚硅氧烷为主体的,并加有中性非增强性填料, $CH_2=CHSiMe$  氨基硅烷及二甲替甲酰胺等的单组份 RTV 硅橡胶,其主要性能如下:

抗张强度

4200 牛顿/米

伸长率

1650 %

邵氏硬度

15

## Method of Preparing Conductive Room Temperature Vulcanizine Material

#### 配制导电室温硫化材料的方法

介绍一种具有触变性的导电室温硫化硅橡胶,分别采用分散在环已烷中的钯粉和醋酐作为导电剂和交联剂。本材料对于高温和 辐射具有稳定性。

#### Silicone Pressure Sensitive Adhesives & Tapes

#### 有机硅压敏胶粘剂及胶粘带

介纸以聚四氟乙烯或聚酯薄膜作背衬的压敏胶粘剂。它是由有机硅树脂八烷基环四硅氧烷的聚合物和 2.4-二氯化苯酰组成, 另加有烷基芳基或烷基芳烷基硅氧烷作为增量剂和增塑剂。

#### Использование силиконовых каучуков и резин для конструирования лекарственных форм 医药用硅橡胶

本文所介绍的硅橡胶适用于作移植材料或内服药胶囊之用。它是低分子量聚二烷基(二芳基)硅氧烷,牌号为 CKTH 文章对它进行综述。

#### Elastomeric Materials for prosthetic Heart Valves

#### 供心脏小球使用的弹性体材料

对三种硅橡胶,一种聚氨酯橡胶及一种天然胶作心脏小球材料的对比试验。结果证明,聚氨酯的效果差于硅橡胶,但优于天然 胶。天然胶的缺点在于易撕裂,而且在现阶段活性太大,不适宜在人体内使用。

#### Rubber & Medicine: The Beat Goes on

#### 通过橡胶和医药使心脏继续跳动下去

本文介绍了一些硅橡胶件埋植人体内的方法以及延长病人寿命、促进病人康复的例子。重点讨论了硅橡胶心脏瓣膜的博跳保持情况,以及硅橡胶人工关节用于恢复关节炎患者的本功能。

# Development of Blood-Compatible Elastomers-Surface Structure & Blood Compatibility of Avcothane Elastomers

#### 对血液有亲和性弹性体的发展-Avcothane 弹性体的表面结构与其血液亲和性

介绍一种医用共聚硅橡胶 Avcothane 它是聚氨酯和聚二烷基硅氧烷的镶嵌共聚物,在不用抗凝血剂处理的情况下就具有显著的血液亲和性,用它作的人工主动脉瓣已已试用于心血管病患者,未发现明显的血液反应。

# Blood Compatibility of Silicone Rubber Chemically Coated With Cross-linked Albumin

#### 经交联蛋白质化学处理的硅橡胶的血液亲和性

介绍一种新的经交联蛋白质化学处理的硅橡胶能改进血液亲和性。经在狗身上做了腔静脉和肾脏抗凝血试验,效果良好。在移 植一星期后其抗凝血性证明比未经处理的硅橡胶好得多。

#### Shear-Induced Hemolysis With Commercial & Glow Discharge Silicones

#### 聚硅氧烷经放电及剪切感应处理后的溶血性研究

作者对 14 种不同的二甲基聚硅氧烷材料进行了溶血特性的研究,结果表明: 大多数聚硅氧烷与聚乙烯相比,其溶血性较低,只及后者的 80% 但经过处理后其溶血性超过聚乙烯 70~280%。

Prefabricated Silicone Subdermal Mandibular Implants Observations & Problems Related to Their Application

#### 颚骨皮下移植用的硅橡胶预制件应用观察及存在问题

颚骨缺损病人整形时采用导体材料存在相当困难,这种困难主要是由于该部位受到连续应力和动作所致。文章介绍用金属线增强的硅橡胶移植体应用于颚骨整形。共作了80例临床试验,其中有的成功,有的失败。移植是通过切除埋置及缝合而完成的。

#### The Biostability of Silicone Rubbers, Polyamide & a Polyester

#### 硅橡胶,一种聚酰胺和一种聚酯的生物稳定性

采用微观、宏观、机械和物化等多种试验方法对四种高温硫化硅橡胶,一种室温硫化硅橡胶以及尼龙-6 和聚对苯二甲酸乙二醇酯的生物降解现象进行研究。并对各该材料长期埋置体内的适用性作了评价。文章还介绍了所采用的试验方法。

#### In Vivo Tissue Reactivity of Radiation-Cured Silicone Rubber Implants

#### 用辐射硫化的硅橡胶埋植体的组织反应

在实验室研究活组织反应的结果表明,硅橡胶纯胶在辐射硫化下的组织反应要比白炭黑填充的同样硅橡胶轻。文章接着提出了强力高组织反应轻的硅橡胶人体埋植件的制造工艺。

# Safety Aspects of Silicone Polymers Used in the Medical Profession

#### 医用有机硅聚合物的安全问题

硅橡胶等有机硅聚合物在医学上虽有广泛应用,但在其安全性的评价上尚存在问题。本文通过动物试验对有机硅聚合物在体内 埋植的毒性问题作了综合性评价。

#### Economic Wire & Cable Construction With Silicone Rubbers

#### 经济的硅橡胶电缝和电缆的构造

介绍在用螺杆压出机压出硅橡胶胶料时应该掌握的工艺操作要点,还对连续硫化和热空气硫化等两种工艺作了对比,并介绍沸腾床硫化工艺用于硅橡胶压出制品的情况。重点叙述了胶料加工和产品制造中遇到故障和问题时应该采取的措施。

#### Silicone Molds 'Save' Sculptur

#### 硅橡胶模制能节省艺术木雕刻时间

硅橡胶作为模制材料是它的新应用之一,本文介绍它用于艺术品的镌刻和雕塑。

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# General Review



#### SILICONE RUBBER—A PERSPECTIVE\*

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It is indeed an honor to have been selected as the Charles Goodyear Medalist in the Bicentennial Year 1976. Previous medalists have truly made the award internationally known. To join their ranks is a double honor, for it is the first time you have recognized work in the area of silicone rubber. Clearly you recognize not only my work, but that of coworkers and many others in the field who have made silicone rubber important far beyond its volume of usage. "Silicone Rubber—a Perspective" is my effort to report on my work and that of others in the perspective of a rapidly developing field of synthetic rubber.

#### INTRODUCTION

The importance of silicone rubber lies in its ability to serve under severe environments where nothing else will function or in its ability to function more reliably in less stringent environments. Simple price economies usually do not favor silicone rubber, for it is higher in price than all but the exotic new rubbers. However, use economics, the service life per dollar, is quite favorable. Moreover, silicone rubber is one of the very few materials whose price has declined steadily over the past twenty years. Beyond economic and functional importance is the area of use in medicine and surgery where the value in terms of life and the quality of life cannot be measured. In perspective then, we will see that the role of silicone rubber in today's world far outweighs its volume usage—roughly 0.2% of all rubber.

#### DISCOVERY

Silicone rubber goes back about 32 years to the middle of World War II. To place this in perspective it is necessary to recall that silicone development, as a new area of polymer research, was opened in the early 1930's. Dr. J. F. Hyde began at this time to seek polymers between the then-known plastics and glass at the Corning Glass Works. Dr. R. R. McGregor and I began silicone research at Mellon Institute in late 1937. Other groups at General Electric began in this period, but I will leave the whole history of silicones in the hands of those who have already written of it<sup>1</sup>.

By 1940 our work at Mellon Institute had progressed to the point where we installed a 20-gallon pressure autoclave to make dimethyldiethoxysilane by an etherless Grignard method in ethylsilicate<sup>2</sup>. Andrianov<sup>3</sup> had indicated such etherless Grignards were possible, but he had not made methyl-substituted silicones. The hydrolysis of these esters gave us polydimethylsiloxanes, and a few years were spent characterizing these materials and learning to polymerize them. Looking back, it is easy to say it took too long, but one must reckon with the state of polymer science at that time as well as with the lack of many

<sup>\*</sup> This paper represents an expanded version of the Charles Goodyear Medal Address—1976, which was delivered at the 109th Meeting of the Rubber Division, American Chemical Society, Minnesota, April 27–30, 1976.

Table I
TODAYS LABORATORY TOOLS NOT AVAILABLE IN 1940

tools now regarded as vital to research. Table I lists a few of the instruments now common in research laboratories which were not available to us in the early 1940's. Recall too that it was war time and priorities were needed even for the magnesium for our Grignards, and red stamps for the edible stearates for our thermostat fluid. I mention these things, not to elicit sympathy for any real or imagined deprived state, but to point out that without sophisticated equipment or techniques, the whole study of silicones was an exciting adventure. Frustrating it was at times, and often slow and thought provoking, but on balance, it was deeply satisfying to find new facts in a totally new world. I wonder if today, surrounded by many new and powerful tools, the researcher doesn't miss the sense of real adventure.

The chemistry of silicones has been discussed many times, but perhaps it is best to show on Figure 1 the polymers we will be talking about and the several routes to their preparation. One begins as we did with methylalkoxysilanes or with methylchlorosilanes and hydrolyzes them in water. The conditions, time, and catalysts all have a bearing on how much "high" polymer forms with hydroxyl ends and how much low polymer cyclics or linears with trimethylsilicon-substituted ends are present. Much time was spent in efforts to polymerize the apparent "linear" polymer before one realized how scrupulously one would have to keep out mono- or trimethyl-substituted silanes. Before long, it was apparent that one could separate the cyclic low polymers by distillations or indeed "crack" the linear high polymer to cyclics with heat alone or with catalysts such as strong alkali. The cyclics then became the preferred raw material to prepare true high polymers for they were inherently free of monoand tri-substituted contaminants. I mention this search for a high polymer before opening the curtain on silicone rubber as such, for it was clear even in the state of polymer chemistry of the early 40's that high polymers were

To put this in perspective, one must recall that Corning Glass Works and Dow Chemical agreed to form a joint company to exploit silicones of all types and Dow Corning came into being in March, 1943. While one of the major objectives of the joint company was to develop insulation for small high-powered electric motors, which Admiral Rickover wanted for his submarines, the first product to reach a real use was the polydimethylsiloxane filled with a small amount of fine-particle silica. This greaselike material was used in the ignition system of planes flying the Atlantic to join the Battle of Britain to prevent corona and loss of ignition, and ultimately loss of planes. At the time of formation of Dow Corning, fluids, greases, and resins were available, but no rubber was being made.

In the course of many polymerization experiments designed to condense terminal hydroxyl groups, we used boric oxide and quickly obtained a strange high polymer. This "bouncing putty" was the precursor of silicone rubber and judging from what frantic mothers later said when calling to learn how to remove "Silly Putty" from their youngster's hair, the title "curser" might have been more applicable. This material was a fun polymer and was a different aspect of our adventure into the world of silicones. It was not a true rubber but it really flowed like a putty and lacked any vulcanization mechanism. We later learned to say it showed rheopexy: solidlike under rapid stress but fluid-like under slow stress.

One more element was necessary before rubber appeared on the scene. In mid-1943, the Bell Telephone Laboratories announced its new Paracon Rubbers. This saturated dibasic acid diester was vulcanized with benzoyl peroxide. It was clear that our saturated polymers also might cure with benzoyl peroxide. Without waiting for a complete solution to the high-polymer problem, I set about to try vulcanization of our low and intermediate molecular weight fluids. It worked, and yet to get a sufficiently high "polymer" to mill and add fillers, it was necessary to make a gel by crosslinking the low polymer with benzoyl peroxide. This "crepe" rubber was then compounded with further benzoyl peroxide and fillers. Vulcanization of this compound yielded a weak rubber—so weak that many managers were not highly impressed. The time was December, 1943.

The mechanism of this vulcanization was not spelled out in the Bell Laboratories' work and it was some time before it was clear to me that it was a free-radical abstraction of hydrogen and the formation of an ethylene link between siloxane chains. Filler studies and vulcanization studies occupied much of my time in the year 1944. Ultimately, this led to my first rubber patent, US 2,460,795, which issued in 1949<sup>6</sup>. Part of this long delay, some of you may recall, was because many patents which were deemed to have significance in wartime were placed under secrecy and only began to issue slowly after the

While these studies to understand the weak rubber was going on, I worked with another Fellowship in Mellon Institute, headed by Dr. E. E. Marbaker.

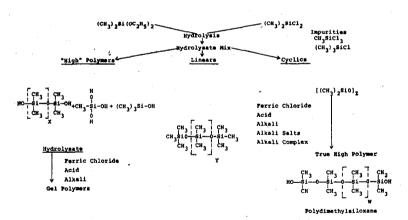


Fig. 1.—Chemistry of formation of polydimethylsiloxanes

His problem was to provide a coating for Navy resistors handling high power levels and subject to rapid temperature fluctuations. Ceramic-coated resistors cracked under the severe environment and in high humidities leaked. One of our pastelike rubber compounds made from an intermediate molecular weight fluid, titanium dioxide filler, and using benzoyl peroxide for vulcanization,

gave a coating which passed all the Navy tests7.

While this was happening, General Electric was also working on silicone rubber and they made a formal announcement in Rubber Ages, in November, 1944. The uses of the new rubber mentioned were as a gasket in turbosuperchargers for B29 bombers and as a gasket in Navy searchlights. The article stated that new and unconventional methods of vulcanization were used, but they could not be disclosed. Patents, which were issued later to General Electric, disclosed methods of polymerization of hydrolyzates involving ferric chloride<sup>9</sup>, of cyclics by ferric chloride<sup>10</sup>, and even curing of the rubber by ferric chloride<sup>11</sup>. The first mention of benzoyl peroxide as the vulcanizing agent was in the patent by Wright and Oliver<sup>9</sup>, which issued in September, 1948. The crepe rubbers used here were quite similar to those used at Mellon Institute in that they were crosslinked prior to compounding and final vulcanization, the only difference being that the crepes derived by G. E. were obtained using ferric chloride polymerization of hydrolyzed chlorosilanes which contained monomethyl- as well as trimethyl-substituted silanes, and ours were from benzoyl-peroxide gelation of intermediate molecular weight fluids.

The commercial rubbers prepared by these techniques had measurable properties that might best be illustrated as in Table II, taken from data sheets issued by Dow Corning in early 194512. These tensile strengths certainly are low, as are the elongations, but, in the light of later knowledge on the effects of polymer molecular weight and chain ends not a part of the network, one could not expect high tensile strengths. The SC stocks prepared from fluid polymers, filler, and benzoyl peroxide but not gelled, all were designed for coating as for the Navy resistors or cloth coating for insulating tapes. The trademark Silastic® began to be used with these first silicone rubbers from

The year 1945 saw the first basic data on silicones released to the public. Prior to this time, publications were largely use oriented and commercial property listings. The Gibson Island Polymer conference invited both General Electric and Dow Corning to send speakers to their summer conference. Dr. Rochow spoke on his newly discovered direct process for the manufacture of methylchlorosilanes from silicon metal and methyl chloride. This was a revolutionary process which moved commercial production away from Grignard reactions. This step forward benefited silicone rubber by decreasing costs and opened the way to large-volume production. I spoke at the same conference on the characteristics of linear and cyclic low-polymer methylsiloxanes. The knowledge of these materials was essential to the purification of cyclics as raw

TABLE II PROPERTIES OF FIRST COMMERCIAL DOW CORNING SILICONE RUBBERS

	SR-73	SR-74
Tensile strength, MPa	1.31	1.44
Elongation, %	115	115
Hardness, Durometer	<b>4</b> 5–50	55–60

#### SILICONE RUBBER

TABLE III
COMMERCIAL SILICONE RUBBER-1946

Stock number	150	160	167	180
Tensile strength, MPa	2.75	4.13	4.13	4.83
Elongation, %	300	200	110	75
Hardness, Durometer	45–55	55–65	55–65	75–80

materials for high molecular weight polydimethylsiloxanes. These data were later published<sup>13</sup> and were confirmed by similar data from General Electric authors<sup>14</sup>.

Efforts to prepare high polymers from cyclics were continuing at Corning Glass Works, Dow Corning Labs, and Mellon Institute. I can only surmise from later publications that similar work was under way at General Electric. A first step in improved high molecular weight polymer was the use of strong acid or alkali on cyclic tetramer of dimethylsiloxane. While the conditions were being worked out, a type of polymerization was run which yielded a pourable polymer. As this polymer remained at room temperature, it became more viscous and ultimately it exhibited gel characteristics. At Dow Corning we called these "K gels". General Electric prepared similar gel polymers using ferric chloride and, at a later date, sold them as SE 76 polymers. Both polymers gelled because conditions during the polymerization were severe enough to remove methyl groups.

These K gels made possible the first step in tensile improvement as we now moved to the range of 400-700 psi., or in today's units 2.75-4.83 MPa, with elongations in the range of 75-300%. These were the properties of a whole new series of rubbers announced by Dow Corning early in 1946<sup>15</sup> (Table III). The stock numbers were 150, 160, 167, and 180, and the fillers for these were Titanox, Celites, calcium carbonate, and zinc oxide. Effort was made to neutralize the polymerization catalyst to avoid depolymerization later, under vulcanization or use conditions. Since these were gels, it is not significant to speak of a molecular weight, but the chain length between crosslinks was greater than in the benzoyl peroxide gels.

An experienced rubber chemist will notice that none of these rubbers contained carbon black—a common filler in his work. Carbon blacks were tried quite early as fillers but, as it happened, an acidic channel black was used. With benzoyl peroxide, no cure could be obtained and indeed, sheets from the mill developed small crystals on the surface while awaiting molding. These proved to be benzoic acid and told us that acidic channel blacks decomposed the benzoyl peroxide. Later, as we became more familiar with carbon blacks, we found that cures could be obtained with benzoyl peroxide if one used alkaline furnace or thermal blacks. Also, as we studied other curing agents, we found that t-butyl perbenzoate as a vulcanizing agent would yield cures even with acidic channel blacks.

Effort was made to block the acidic functions of the channel blacks by treating the filler with methylchlorosilanes. Treatments were obtained, but the acidic blacks continued to prevent vulcanization. However, aging of any vulcanized carbon-black-filled rubbers at temperatures around 200°C gave poorer properties than those from simple inorganic metal oxides and carbonates. Today, carbon black is used only for conductive rubbers and in other very specialized uses.